A Final Report

Grant No. NAG-1-419 Supp. #3

A STUDY OF THE APPLICABILITY OF NUCLEATION THEORY TO QUASI-THERMODYNAMIC TRANSITIONS OF SECOND AND HIGHER EHRENFEST-ORDER

Submitted to:

National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Attention: Dr. Noel T. Wakelyn (Project Manager)
MD M/S 226B

Submitted by:

R. E. Barker, Jr.
Professor

K. W. Campbell
Research Assistant

Report No. UVA/528230/MS87/103

July 1986

SCHOOL OF ENGINEERING AND APPLIED SCIENCE

DEPARTMENT OF MATERIALS SCIENCE

UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA 22901

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FOREWORD

The research described in this report was initiated under NASA-Research Grant NAG-1-419, entitled "A Study of the Applicability of Nucleation Theory to Quasi-Thermodynamic Transitions of Second and Higher Ehrenfest-Order." The work was performed in the Materials Science Department at the University of Virginia, and was administered under the direction of NASA Technical Officer, Dr. Noel T. Wakelyn, of the Langley Research Center. The investigators for this project were Prof. R. Edward Barker, Jr., principal investigator, and Kenny W. Campbell, graduate research assistant. The University Account No. for the project was UVA-5-28230.

This report covers research performed from December 1983 to May 1986.

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SECTION I

ABSTRACT

In this report, a summary of research supported by NASA Grant Number NAG-1-419 is given. The work includes an investigation of the applicability of nucleation theory to second and higher order thermodynamic transitions in the Ehrenfest sense, and a number of significant conclusions relevant to first order transitions, as well. The underlying theoretical method consisted of expanding the Gibbs' free energy in a Maclarin or Taylor series and then using fundamental thermodynamic relations to relate the coefficients to experimentally determinable quantities, and interpreting the results. Work was done on the existence and interpretation of an interfacial energy between "phases" in a second order transition in addition to an investigation of the solid-liquid interfacial energy for various polymers. Extensive considerations have been devoted to various aspects of a particular polymer, polyvinylidene fluoride (PVDF or PVF_2), including an experimental investigation of the effects of an applied electric field on the morphology of melt crystallization and on the nucleation and growth of polarized domains. Some related cooperative work has been carried out with other researchers on the dielectric properties of various materials including polymer solids and oligomeric liquids.

SECTION II

INTRODUCTION

The research described in this final report consists of a number of interconnecting research paths all of which deal in some way with phase or state transitions as the unifying theme in various types of systems. Both theoretical and experimental work has been undertaken and an attempt has been made to connect various aspects of the research from both points of view. In this report a brief summary of work undertaken with support from this grant is given followed by manuscripts and abstracts which give details and a fuller view of the work.

SECTION III

PROGRESS, PUBLICATIONS AND PRESENTATIONS

A. SUMMARY OF COMPLETED WORK

1. Application of Classical Nucleation Theory to Second Order Thermodynamic Transitions in the Ehrenfest Sense.

A formalism has been developed which breaks from the standard approximations of classical nucleation theory (CNT) for the evaluation of the Gibbs' free energy change corresponding to the transformation of a small amount of phase matrix into a small nucleus of β-phase. In this approach, the bulk thermodynamic value, $\Delta G = G_\beta - G_\alpha$, and therefore g, where $g \equiv (G_\beta - G_\alpha)/v_\beta$, can be expanded in a Maclaurin series with respect to a variable representing an external influence on the system. Various expansions have been evaluated corresponding to systems subject to undercooling, hydrostatic pressure, uniaxial tensile stress, and external magnetic or electric fields.

After expanding g in a Maclaurin series, the resulting coefficients are then determined by using thermodynamic relations, by means of which fairly simple expressions for the critical nucleus size r_c and the critical free energy barrier ΔG. These expressions give (1) correction terms which are non-linear functions of T, p, etc. for first order thermodynamic transitions (in the Ehrenfest sense), (2) the size and barrier height for second order transitions, and (3) the method, for a formal extension of nucleation theory to even higher order transitions, which is straight forward in principle but complicated in algebraic expression.

Publications giving details of the expansions as well as the final expressions for r_c and Δ_c for both first and second order transitions for systems undergoing temperature supercooling, subjected to hydrostatic pressure, to tensile stress, or to the application of an electric field are included in the Appendix.

2. Estimation of Interfacial Energies

A major concern which arises from the attempt to apply CNT to second order thermodynamic transitions is the necessity of a non-zero effective interfacial energy between the two "phases". The assumption was made early in this work that γ would be a small quantity (perhaps 1 to 5 mJ/m^2) but effort was needed in order to understand physically how γ could take on non-zero values for the interface about a nucleus undergoing a second order transition. One possible situation occurs when the system undergoing the second order transition is supercooled below the normal second order transition temperature. In this case, as seen in Fig. 1, there appears to be an interfacial energy which depends on the degree of supercooling. When data for polystyrene are extropolated into the supercooled region, the apparent interfacial energy which is obtained agrees with the expected magnitude of γ.

In the course of this work on the effective interfacial energy for a second order phase transition considerable data were found on the surface tension of solid and liquid polymers but there were very few data on the solid-liquid interfacial energy γ_{SL}. Because of the experimental difficulty in obtaining this quantity an attempt was made to theoretically evaluate γ_{SL}. This work was described in detail in the Annual Report on Grant No. NAG-1-419-2 (July 1985) and the results were presented at the May 1984 meeting of the the Virginia Academy of Science (see abstract in Appendix) and are summarized in Figs. 2-4.

3. The Effect of an Electric Field on Ferroelectric Polymers

As a result of the theoretical research on the consequences of an applied electric field on r_c and Δ_c for both first and second order transitions, further investigation was made of these effects on a particular material. The material chosen for investigation was Polyvinylidene Fluoride (PVF_2) because it undergoes both a liquid-crystalline transition and a ferroelectric transition, and has many other important characteristics.

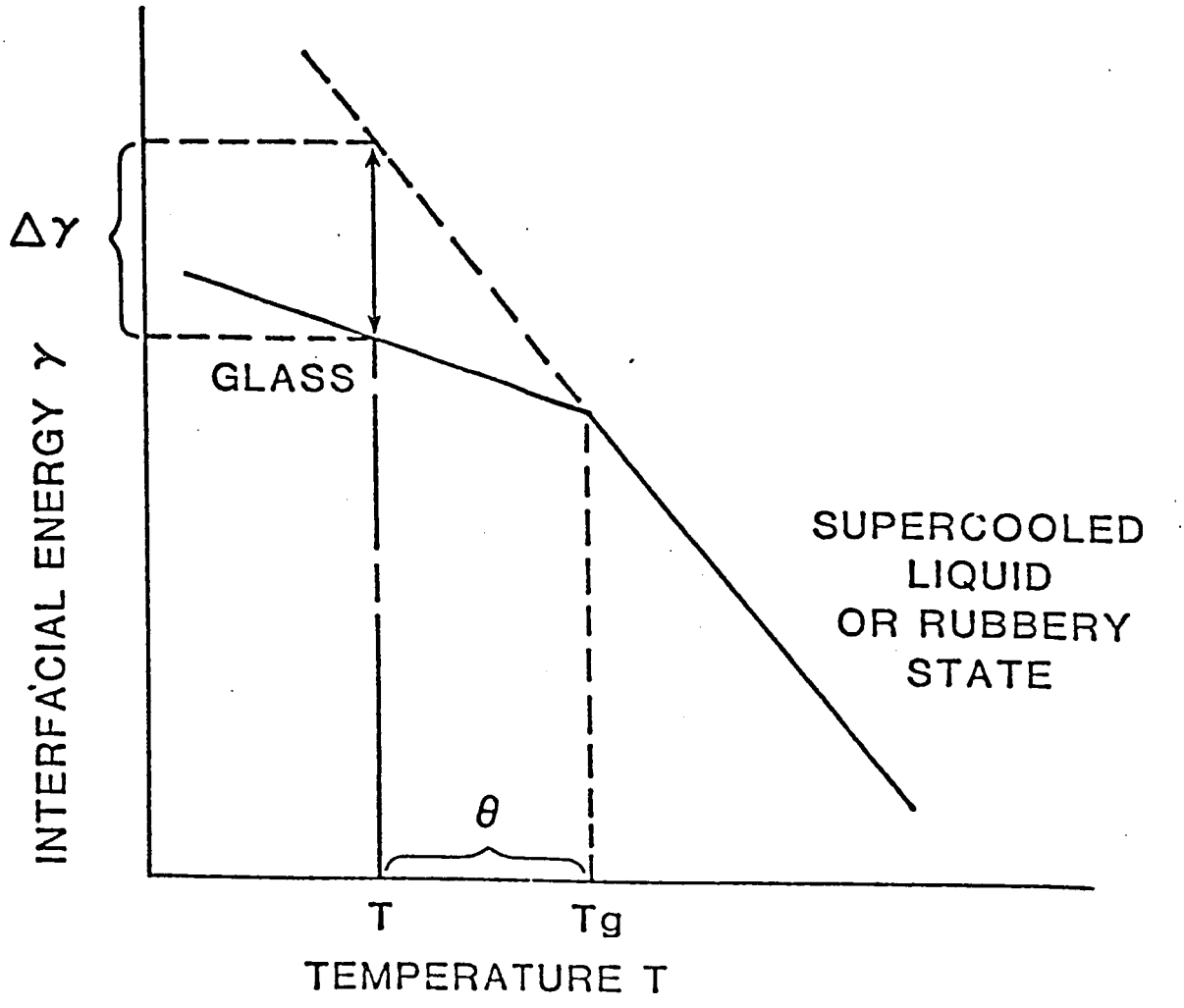

Figure 1. Schematic representation of a method to estimate the effective interfacial energy for an undercooled system if $\gamma_g = \gamma_r$.

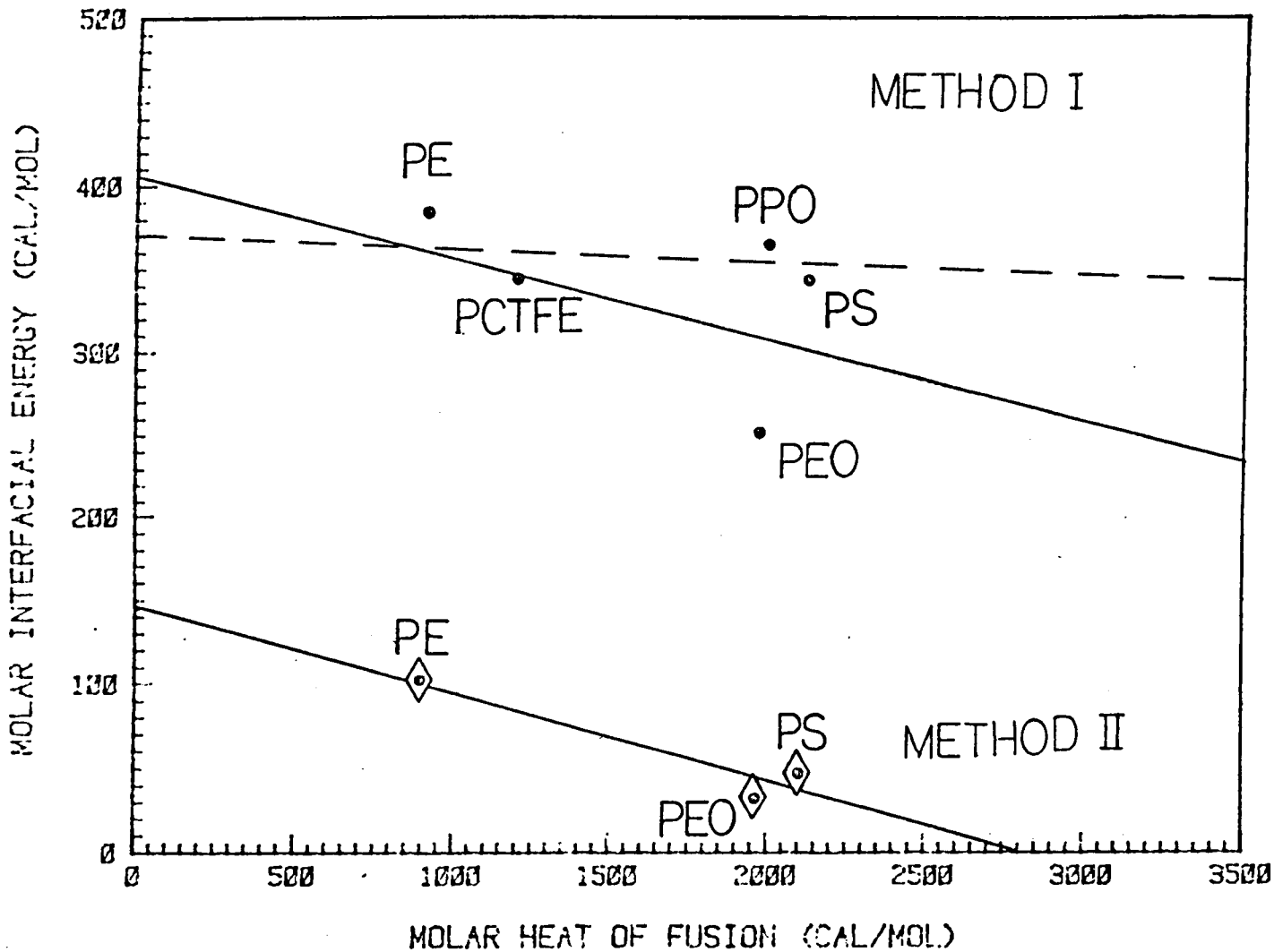

Figure 2. The relationship between the molor interfacial energy and the molar heat of fusion for various polymers calculated using (i) Method I where $\gamma_{SL} = \gamma_L$ and (ii) Method II where

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^d\gamma_L^d}{\gamma_S+\gamma_L} - \frac{4\gamma_S^p\gamma_L^p}{\gamma_S+\gamma_L}$$

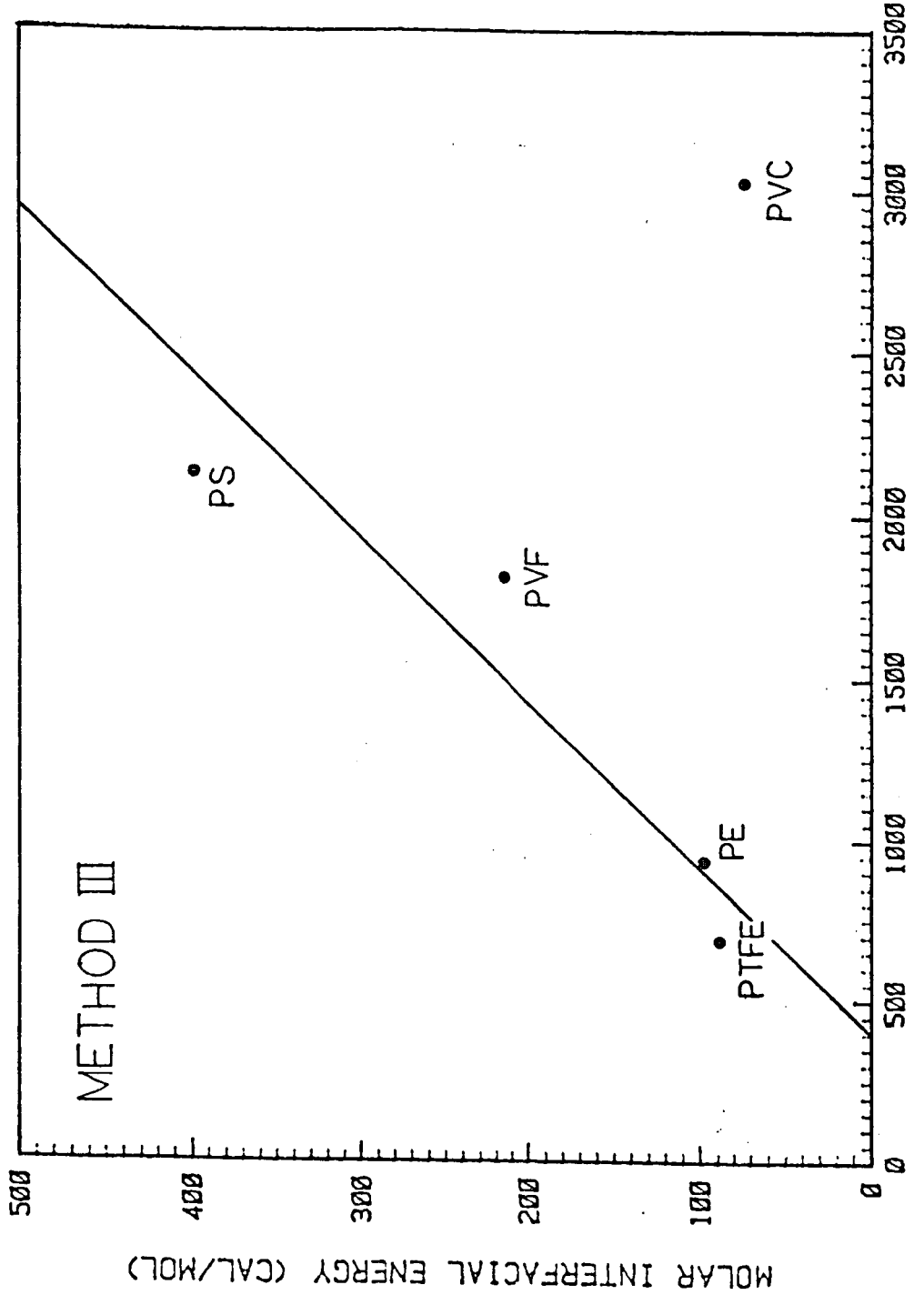

Figure 3. (iii) Method III where $\gamma_{SC} = \gamma_S - \gamma_C$.

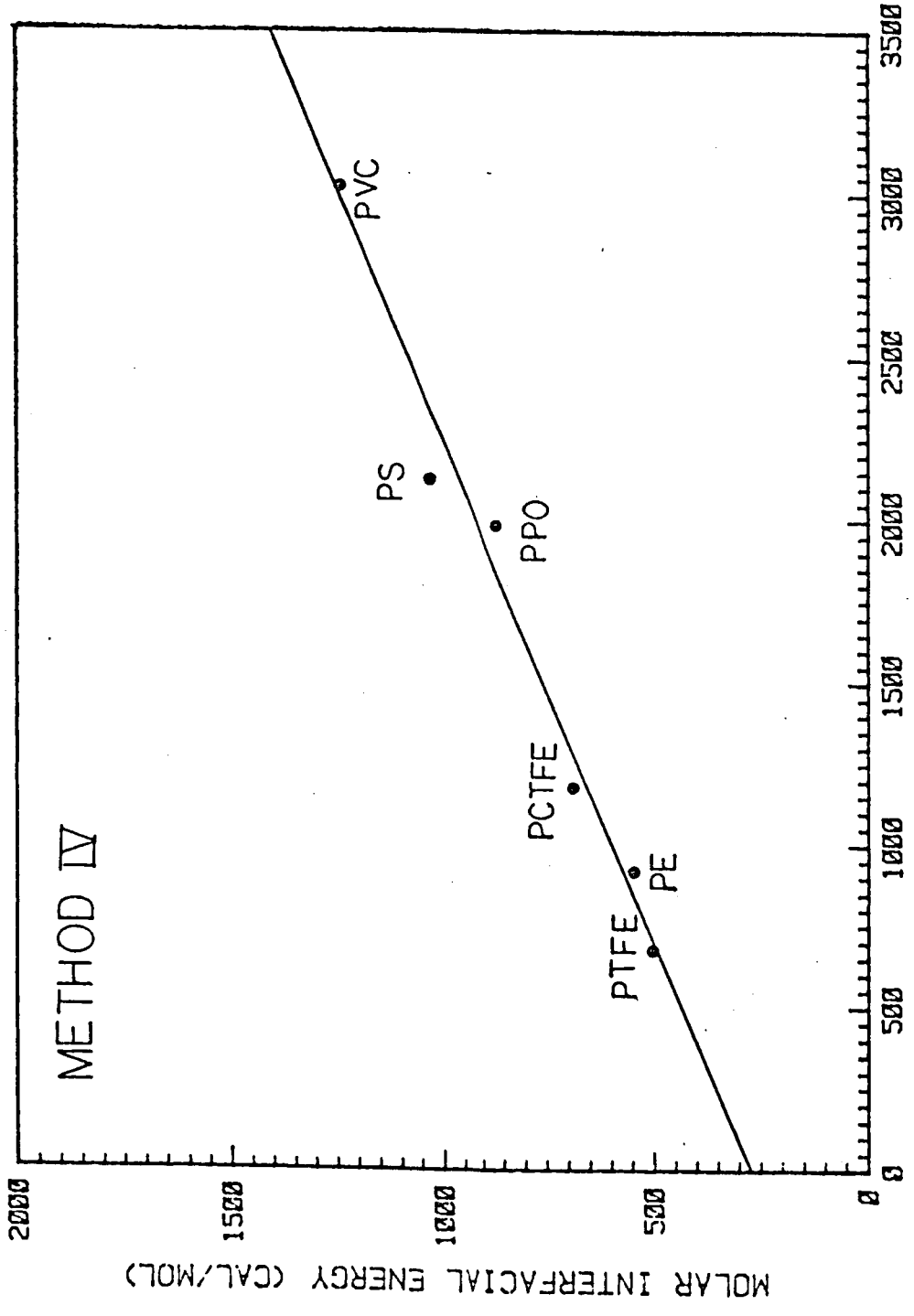

Figure 4. (iv) Method IV where the method of Turnbull[16] is used to estimate γ_{SC} from nucleation theory.

An experimental investigation was undertaken to observe the effects of an electric field on the crystallization of PVF_2 from the melt. In this work a thin film PVF_2 sample is melted between two electrodes. After holding above T_m for approximately. 15 minutes an electric field is applied across the sample. The sample is then cooled to a temperature about 40° lower than T_m and held at this temperature with the electric field remaining on for a period of approximately 1 hour. The sample then is cooled rapidly to room temperature and the resulting microstructure is compared by means of an optical microscope with that of a sample similarly heat treated but without the applied field. Many samples were studied with only a small effect due to the field but this is believed to be the result of an insufficient field strength due to arcing across the sample. Remedies to inhibit the arcing and thus achieve a higher field and therefore a more dramatic effect on morphology are now being investigated. For theoretical reasons it is expected that the effect will depend on the square of the field intensity.

Further theoretical studies of PVF_2 concerned the nucleation and growth of polarized domains. These domains consist of groups of dipoles aligned in a common direction. Details of the theoretical investigation on the nucleation of polarized domains are given in a paper submitted for publication which is included in the Appendix.

4. Modified Johnson-Mehl-Avrami Treatment of Crystallization Kinetics to Investigate Domain Nucleation and Growth

To better understand the mechanism by which the nucleation and growth of polaraized domains occurs, the standard Johnson-Mehl-Avrami (JMA) treatment of crystallization kinetics is modified to be applicable to polarization domains. In the classical JMA treatment, the degree of crystallirity is measured as a function of time and appropriate data are manipulated to achieve a plot of

$\ell n\ell n[(\upsilon_\infty - \upsilon_o)/(\upsilon_\infty - \upsilon_t)]$ vs ℓn (time) where υ is the volume of the fully crystallized sample, υ_o is the volume of the fully amorphous sample and v_t is the volume at any time t. The resulting curves have a large linear region the slope of which is used to infer the shape of the nucleus, the type of nucleation, and the growth controlling mechanism as indicated in Table 1. The JMA treatment was modified in order to be useful in the study of polarization domains. In this approach the resulting plot is $\ell n\ell n\,[(P_\infty - P_o)/(P_\infty - P_t)]$ vs ℓnt where P_∞ is the saturation polarization, P_o is the initial polarization, and P_t is the polarization at any time t. It is believed that slopes of the resulting curves on this plot describe the nucleation and growth of the polarized domains. Some results of this work were presented at the May 1985 meeting of the Virginia Academy of Science (see abstract in the Appendix).

5. Investigation of the Dielectric Properties of Various Materials

Due to the appearance of the dielectric constant terms in the expansion of the free energy for a system under the influence of an external electric field, work has been done, and is continuing in collaboration with other researchers, on the dielectric properties of polymeric materials. A Time Domain Dielectric Spectroscopy System (TDDS) is used in this work and research is being done on both solid and liquid polymers as well as polymers blends and systems undergoing phase separation and phase transitions.

A portion of this work was presented at the March 1986 meeting of the American Physical Society (see abstract in the Appendix) in which a model describing the dielectric relaxation of a series of alcohols was developed which agrees extremely well with the results obtained experimentally with the TDDS system. The details of this model are given in a paper, submitted for publication, included in the Appendix.

B. PUBLICATIONS AND PRESENTATIONS

Papers

1. Barker, R. E., Jr., and Campbell, K. W., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions," J. Appl. Phys. 56 (9), 2386 (1984).

2. Campbell, K. W., and Barker, R. E., Jr., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions: II. Effects Pressure and Stress." Society of Plastics Engineers Journal: Polymer Engr. and Sci. 25 (17) (1985).

3. Campbell, K. W., Barker, R. E., Jr., and Huang, C. C., "Domain Growth in Polyvinylidene Fluoride Considered in Terms of Ehrenfest Transitions and Nucleation Theory," to be published in J. Polym. Sci pending acceptance. (Manuscript Appended)

4. Huang, C. C., Campbell, K. W., Barker, R. E., Jr., "A Simple Tumbling Model for the Dielectric Relaxation of a Series of Oligomeric Alcohols," to be published pending acceptance. (Manuscript Appended)

5. Barker, R. E., Jr., Campbell, K. W., Huang, C. C., Ross, C. D., "Time Domain Dielectric Spectroscopy as a tool to Study Phase Nucleation Processes," to be published in the 1986 Annual Report of the Conference on Electrical Insulation and Dielectric Phenomenon, publ. by IEEE Nov. 1986.

Abstracts

A1. Barker, R. E., Jr., and Campbell, K. W., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions," Bull. Am. Phys. Soc. 29 (No. 5), 932 (1984).

A2. Campbell, K. W., and Barker, R. E., Jr., "Considerations of the Ratio of Interfacial Energy to Specific Enthalpy of Melting for Various Classes of Materials," Va. J. Sci. 35 (No. 2), 126 (1984).

A3. Barker, R. E., Jr., Campbell, K. W., and Huang, C. C., "Domain Growth in Polyvinylidene Flouride Considered in Terms of Ehrenfest Transitions and Nucleation Theory," Bull. Am. Phys. Soc. 30 (No. 3), 187 (1985).

A4. Campbell, K. W., Barker, R. E., Jr., and Huang, C. C., "Kinetic Aspects of Electric Polarization in Ferroelectric Polymers," Va. J. Sci. 36 (2), 154 (1985).

A5. Huang, C. C., Campbell, K. W., and Barker, R. E., Jr., "Interactions of Polar Diffusants with Polymers as Inferred by Time Domain Dielectric Spectroscopy," Bull. Am. Phys. Soc. 31 (3), 514 (1986).

Presentations

Barker, R. E., Jr., and Campbell, K. W., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions," presented at the Detroit Meeting of the American Physical Society, March 26-30, 1984, Detroit, Michigan.

Campbell, K. W., and Barker, R. E., Jr., "Considerations of the Ratio of Interfacial Energy to Specific Enthalpy of Melting for Various Classes of Materials," presented at the Virginia Academy of Science Meeting, May 17, 1984, Richmond, Virginia.

Campbell, K. W., and Barker, R. E., Jr., "Predictions of Nucleation Theory Applied to Ehrenfest Thermodynamic Transitions: I," presented at the Symposium on Applications of Phase Diagrams in Polymer Science, National Bureau of Standards, Washington, D. C., October 15-17, 1984.

Barker, R. E., Jr., Campbell, K. W., and Huang, C. C., "Domain Growth in Polyvinylidene Flouride Considered in Terms of Ehrenfest Transitions and Nucleation Theory," presented at the March 25-29, 1985 meeting of the American Physical Society in Baltimore, Md. (Manuscript Appended).

Campbell, K. W., Barker, R. E., Jr., and Huang, C. C., "Kinetic Aspects of Electric Polarization in Ferroelectric Polymers," presented at the 63rd Annual Meeting of the Virginia Academy of Science, May 15-17, 1985, College of William and Mary, Williamsburg, Virginia.

Huang, C. C., Campbell, K. W., and Barker, R. E., Jr., "Interactions of Polar Diffusants with Polymers as Inferred by Time Domain Dielectric Spectroscopy," presented of the meeting of the American Physical Society, March 30-April 4, 1986, Las Vegas, Nevada.

Ross, C. D., Huang, C. C., and Barker, R. E., Jr., "Time Domain Spectroscopy as a tool to Study Phase Nucleation PRocesses." Presented at the 64th Annual Meeting, Virginia Academy of Science, May 15, 1986, James Madison University, Harrisonburg, Va. (Abstract Appended)

Barker, R. E., Jr., Huang, C. C., Ross, C. D., and Campbell, K. W., "Time Domain Dielectric Spectroscopy as a Tool to Study Phase Nucleation Processes," to be presented at 55th Annual Meeting of the Conference on Electrical Insulation and Dielectric Phenomena, November 2-6, 1986, Claymont, DE.

IV. SUMMARY AND COMMENTS

The original main thrust of this research was to explore the theoretical consequences of trying to apply the concepts of nucleation theory to second order thermodynamic transitions (the order being defined as that of the smallest order partial derivative $(\partial^n G/\partial T^n)$ which is discontinuous). An intensive investigation led to interesting and useful results for second order transitions for the special cases of (1) undercooling at constant pressure, (2) the application of hydrostatic pressure at constant temperature, (3) the application of tensile stress, and (4) the application of an electric field. The initial work uncovered some fundamental unresolved problems, e.g., those connected with the interfacial energies between the phases, and also pointed to important possible improvements in the analysis of the kinetics of first order growth processes. Efforts to apply ideas developed in the work to several problems of interest in polymer science looked quite promising at the termination of Grant NAG-1-419. One important new thrust upon which considerable progress was being made is the "switching behavior" of ferroelectric polymers such as polyvinylidene fluoride (which has at least six solid phases and is therefore an especially good candidate for the experimental investigation of our theoretical approach). We feel that within the limited budgetary constraints that quite a lot was accomplished in this research and we hope that a continuation will soon be possible.